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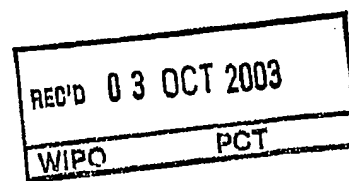
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出願年月日  
Date of Application: 2003年 2月14日

出願番号  
Application Number: 特願2003-037435

[ST. 10/C]: [JP2003-037435]

出願人  
Applicant(s): 山口 猛央

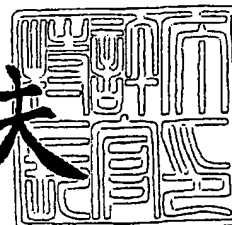


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Appln. No. 2003-037435

Your Reference: 03234.3029

[Name of Document] Specification

[Title of the Invention] Electrode for Fuel Cell, Fuel Cell  
Using the Electrode and Method for Producing the Same

[CLAIMS]

[Claim 1] An electrode for fuel cell comprising a porous electron-conductive material carrying a catalyst, wherein a proton-conductive polymer is arranged on a surface, including surfaces of pores, of the porous electron-conductive material or in the vicinity of the surface, and the proton-conductive polymer is obtained by carrying out polymerization of a proton-conductive monomer or an equivalent thereto on the surface or in the vicinity thereof.

[Claim 2] The electrode for fuel cell according to claim 1, wherein the catalyst is a noble metal catalyst.

[Claim 3] The electrode for fuel cell according to claim 1 or 2, wherein the catalyst is Pt or Pt-Ru.

[Claim 4] The electrode for fuel cell according to any one of claims 1 to 3, wherein the porous electron-conductive material is a carbon-based porous electron-conductive material.

[Claim 5] The electrode for fuel cell according to claim 4, wherein the carbon-based porous electron-conductive material is selected from the group consisting of carbon black, acetylene black, graphite, carbon fiber, carbon nanotube, fullerene, activated carbon and glass carbon.

[Claim 6] The electrode for fuel cell according to any one of claims 1 to 5, wherein the pores have the average diameter of 10  $\mu\text{m}$  or less.

[Claim 7] The electrode for fuel cell according to any one of claims 1 to 6, wherein the proton-conductive polymer is

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not caused to flow out by a cell power generation operation from the surface of the porous electron-conductive material or in the vicinity thereof.

[Claim 8] The electrode for fuel cell according to any one of claims 1 to 7, wherein one end of the proton-conductive polymer is bound to the surface of the porous electron-conductive material through a chemical bond.

[Claim 9] The electrode for fuel cell according to any one of claims 1 to 8, wherein the proton-conductive polymer has a hydrophobic site, and the polymer is adsorbed in a hydrophobic manner to the surface of the porous electron-conductive material via the hydrophobic site.

[Claim 10] A fuel cell having an electrode for fuel cell according to any one of claims 1 to 9.

[Claim 11] A solid polymer fuel cell having an electrode for fuel cell according to any one of claims 1 to 9.

[Claim 12] An electrode for fuel cell, comprising the steps of:

- a) causing a catalyst to be carried on a porous electron-conductive material;
- b) forming a proton-conductive polymer on a surface, including surfaces of pores, of the porous electron-conductive material or in the vicinity thereof by carrying out polymerization of a proton-conductive monomer; and
- c) transforming the porous electron-conductive material into an assembly,

wherein the steps can be changeable in the order thereof.

[Claim 13] A method for producing an electrode for fuel cell, comprising the steps of:

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- a) causing a catalyst to be carried on a porous electron-conductive material; thereafter,
- b) forming a proton-conductive polymer on a surface, including surfaces of pores, of the porous electron-conductive material or in the vicinity thereof by carrying out polymerization of a proton-conductive monomer; and then,
- c) transforming the obtained porous electron-conductive material into an assembly.

[Claim 14] A method for producing an electrode for fuel cell, comprising the steps of:

- a) causing a catalyst to be carried on a porous electron-conductive material; thereafter,
- c) transforming the obtained porous electron-conductive material into an assembly; and then,
- b) forming a proton-conductive polymer on a surface, including surfaces of pores, of the obtained porous electron-conductive material or in the vicinity thereof by carrying out polymerization of a proton-conductive monomer.

[Claim 15] A method for producing an electrode for fuel cell, comprising the steps of:

- b) forming a proton-conductive polymer on a surface, including surfaces of pores, of a porous electron-conductive material or in the vicinity thereof by carrying out polymerization of a proton-conductive monomer; thereafter,
- a) causing a catalyst to be carried on the obtained porous electron-conductive material; and then,
- c) transforming the obtained porous electron-conductive material into an assembly.

[Claim 16] A method for producing an electrode for fuel cell, comprising the steps of:

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- b) forming a proton-conductive polymer on a surface, including surfaces of pores, of a porous electron-conductive material or in the vicinity thereof by carrying out polymerization of a proton-conductive monomer; thereafter,
- c) transforming the obtained porous electron-conductive material into an assembly; and then,
- a) causing a catalyst to be carried on the obtained porous electron-conductive material.

[Claim 17] A method for producing an electrode for fuel cell, comprising the steps of:

- c) transforming a porous electron-conductive material into an assembly; thereafter,
- a) causing a catalyst to be carried on the porous electron-conductive material, which is a part of the assembly; and then,
- b) forming a proton-conductive polymer on a surface, including surfaces of pores, of the porous electron-conductive material or in the vicinity thereof by carrying out polymerization of a proton-conductive monomer.

[Claim 18] A method for producing an electrode for fuel cell, comprising the steps of:

- c) transforming a porous electron-conductive material into an assembly; thereafter,
- b) forming a proton-conductive polymer on a surface, including surfaces of pores, of the porous electron-conductive material, which is a part of the assembly, or in the vicinity thereof by carrying out polymerization of a proton-conductive monomer; and then,
- a) causing a catalyst to be carried on the porous electron-conductive material.

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[Claim 19] The method according to any one of claims 12 to 18, wherein the assembly is a catalyst layer formed on one or both of the electrodes for fuel cell.

[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Pertains]

The present invention generally relates to an electrode for fuel cell, for example, an electrode for solid polymer fuel cell; a fuel cell using the electrode, for example, a solid polymer fuel cell; and a method for producing the electrode and the fuel cell.

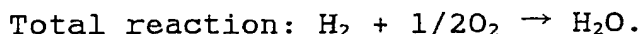
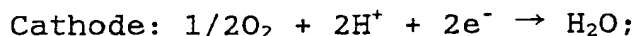
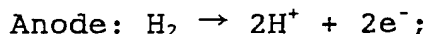
[0002]

[Prior Art]

There have been the needs to build up a fuel cell having higher energy conversion efficiency and less emission of NO<sub>x</sub> or SO<sub>x</sub>, in order to deal with environment and energy issues. In particular, a solid polymer fuel cell (PEFC or Polymer Electrolyte Fuel Cell) has excellent characteristics of a low temperature operation at a high output density and water generation only in power generation reaction. Further, there have been the needs to build up a direct methanol fuel cell (DMFC or Direct Methanol Polymer Fuel Cell) directly using methanol, which is excellent in portability as a fuel.

[0003]

With respect to the above-described fuel cells, it has been desired to solve reduction in performance caused by the following electrode reaction:



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It has been considered that the problem can be solved by efficiently arranging three-phase interfaces in an electrode through which donation and acceptance of reacting substances (for example,  $H_2$ ,  $O_2$  and the like), protons ( $H^+$ ) and electrons ( $e^-$ ) can be performed at the same time.

[0004]

A construction of a fuel cell is such that an anode and a cathode are generally arranged so that an electrolyte is sandwiched between the electrodes. The electrodes have respective electrode catalyst layers if desired. As a method for producing the electrode catalyst layers, there has been available a method in which a mixed solution of a catalyst-carrying carbon black and a proton conductive polymer such as Nafion (registered trademark) is directly coated on an electrolyte (for example, see M. S. Wilson et al., J. Electrochem. Soc. 139(2) (1992) 28-30). In the method, however, only a part of the catalysts carried on the carbon black is actually used for three-phase interfaces, so that a performance depending on a catalyst quantity has not been exerted.

[0005]

As means for efficiently arranging the three-phase interfaces, for example, it is considered to increase an introduced amount of the catalysts in an electrode reaction. As a catalyst, however, a noble metal such as Pt has been generally used. Thus, increased amount of the catalysts leads to a problem of significantly increased cost.

[0006]

Another means for efficiently arranging the three-phase interfaces with a suppressed amount of the catalyst is

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disclosed in Japanese Laid-open Publication No. 2002-100374 and the like. This publication discloses that a cation exchange resin and a catalyst are provided on surfaces of carbon particles, and that the catalyst is arranged in the vicinity (site X) of a portion of the cation exchange resin in contact with the surface of the carbon particles. That is, the means disclosed in Japanese Laid-open Publication No. 2002-100374 is to efficiently provide the three-phase interfaces by arranging a suppressed amount of the catalyst at the site X. However, this method cannot efficiently arrange both phases in an arbitrary manner, since a catalyst carrying site depends on a polymer placement site in the method. Therefore, the method contributes to a suppressed amount of the catalyst introduced, whereas it is impossible to efficiently control the structure of a catalyst layer.

[0007]

[Problem to be Solved by the Invention]

Accordingly, a purpose of the present invention is to provide an electrode for fuel cell, for example, an electrode for solid polymer fuel cell, in which three-phase interfaces are efficiently arranged in the electrode and the electrode has improved fuel cell characteristics.

In addition to the above-mentioned purpose, another purpose of the present invention is to provide a fuel cell having the electrode for fuel cell, for example, a solid polymer fuel cell.

Further, in addition to, or other than the above-mentioned purpose, a purpose of the present invention is to provide a method for producing the electrode for fuel cell and a fuel cell having the electrode therein.



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[0008]

[Means for Solving Problem]

The present inventors have conducted intensive studies with the result that the following matters have been found. That is, a catalyst is carried on an electron-conductive material such as carbon black as in the prior art, and the catalyst is also disposed in primary pores of the nanometer order to the micrometer order made of carbon black. Thereafter, a monomer and the like is disposed on a surface (including surfaces of primary pores) of the obtained catalyst-carrying carbon black, and then, the monomer and the like is polymerized to thereby form a proton-conductive polymer. By disposing a proton-conductive polymer obtained from a monomer and the like in such a manner and a catalyst in primary pores, the three-phase interfaces can be arranged in the primary pores (in other words, "on a microscopic scale"). Usage of primary particles, each of which has the three-phase interfaces formed on a microscopic scale, secondary particles thereof or an assembly of the primary and secondary particles as an electrode for fuel cell enables an electrode for fuel cell and a fuel cell having more improved characteristics to be obtained.

[0009]

Specifically, the inventors have found the following inventions.

<1> An electrode for fuel cell comprising a porous electron-conductive material carrying a catalyst, wherein a proton-conductive polymer is arranged on a surface, including surfaces of pores, of the porous electron-conductive material or in the vicinity of the surface, and the proton-

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conductive polymer is obtained by carrying out polymerization of a proton-conductive monomer or an equivalent thereto on the surface or in the vicinity thereof.

[0010]

<2> In the above item <1>, the catalyst may be a noble metal catalyst, and preferably the catalyst may comprise a platinum group.

<3> In the above item <1> or <2>, the catalyst may be Pt or Pt-Ru.

[0011]

<4> In any one of the above items <1> to <3>, the porous electron-conductive material may be a carbon-based porous electron-conductive material.

<5> In the above item <4>, the carbon-based porous electron-conductive material may be selected from the group consisting of carbon black, acetylene black, graphite, carbon fiber, carbon nanotube, fullerene, activated carbon, and glass carbon.

[0012]

<6> In any one of the above items <1> to <5>, the pores may have the average diameter of 10  $\mu\text{m}$  or less, preferably 1 nm to 1  $\mu\text{m}$ , more preferably 1 nm to 100 nm.

<7> In any one of the above items <1> to <6>, the proton-conductive polymer may be not caused to flow out by a cell power generation operation from the surface of the porous electron-conductive material or in the vicinity thereof, in particular from inside the pores thereof. For example, the proton-conductive polymer may be not caused to flow out by water from the surface of the material or in the vicinity thereof, in particular from inside the pores thereof.

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[0013]

<8> In any one of the above items <1> to <7>, one end of the proton-conductive polymer may be bound to the surface of the porous electron-conductive material through a chemical bond.

<9> In any one of the above items <1> to <8>, the proton-conductive polymer may have a hydrophobic site, and the polymer may be adsorbed in a hydrophobic manner to the surface of the porous electron-conductive material via the hydrophobic site.

[0014]

<10> A fuel cell having an electrode for fuel cell described in any one of the above items <1> to <9>.

<11> A solid polymer fuel cell having an electrode for fuel cell described in any one of the above items <1> to <9>.

<12> A direct methanol solid polymer fuel cell having an electrode for fuel cell described in any one of the above items <1> to <9>.

[0015]

<13> An electrode for fuel cell, comprising the steps of: a) causing a catalyst to be carried on a porous electron-conductive material; b) forming a proton-conductive polymer on a surface, including surfaces of pores, of the porous electron-conductive material or in the vicinity thereof by carrying out polymerization of a proton-conductive monomer; and c) transforming the porous electron-conductive material into an assembly, wherein the steps can be changeable in the order thereof.

[0016]

<14> A method for producing an electrode for fuel cell, comprising the steps of: a) causing a catalyst to be carried

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on a porous electron-conductive material; thereafter, b) forming a proton-conductive polymer on a surface, including surfaces of pores, of the porous electron-conductive material or in the vicinity thereof by carrying out polymerization of a proton-conductive monomer; and then, c) transforming the obtained porous electron-conductive material into an assembly.

[0017]

<15> A method for producing an electrode for fuel cell, comprising the steps of: a) causing a catalyst to be carried on a porous electron-conductive material; thereafter, c) transforming the obtained porous electron-conductive material into an assembly; and then, b) forming a proton-conductive polymer on a surface, including surfaces of pores, of the obtained porous electron-conductive material or in the vicinity thereof by carrying out polymerization of a proton-conductive monomer.

[0018]

<16> A method for producing an electrode for fuel cell, comprising the steps of: b) forming a proton-conductive polymer on a surface, including surfaces of pores, of a porous electron-conductive material or in the vicinity thereof by carrying out polymerization of a proton-conductive monomer; thereafter, a) causing a catalyst to be carried on the obtained porous electron-conductive material; and then, c) transforming the obtained porous electron-conductive material into an assembly.

[0019]

<17> A method for producing an electrode for fuel cell, comprising the steps of: b) forming a proton-conductive

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polymer on a surface, including surfaces of pores, of a porous electron-conductive material or in the vicinity thereof by carrying out polymerization of a proton-conductive monomer; thereafter, c) transforming the obtained porous electron-conductive material into an assembly; and then, a) causing a catalyst to be carried on the obtained porous electron-conductive material.

[0020]

<18> A method for producing an electrode for fuel cell, comprising the steps of: c) transforming a porous electron-conductive material into an assembly; thereafter, a) causing a catalyst to be carried on the porous electron-conductive material, which is a part of the assembly; and then, b) forming a proton-conductive polymer on a surface, including surfaces of pores, of the porous electron-conductive material or in the vicinity thereof by carrying out polymerization of a proton-conductive monomer.

[0021]

<19> A method for producing an electrode for fuel cell, comprising the steps of: c) transforming a porous electron-conductive material into an assembly; thereafter, b) forming a proton-conductive polymer on a surface, including surfaces of pores, of the porous electron-conductive material, which is a part of the assembly, or in the vicinity thereof by carrying out polymerization of a proton-conductive monomer; and then, a) causing a catalyst to be carried on the porous electron-conductive material.

[0022]

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<20> In any one of the above items <13> to <19>, the step b) may have a modification step of modifying the surface of the porous electron-conductive material.

<21> In the above item <20>, the modification step may be inserted before the proton-conductive monomer is disposed on the surface, including surfaces of pores, of the porous electron-conductive material or in the vicinity thereof, or after the monomer is disposed and before forming the polymer.

[0023]

<22> A method for producing a fuel cell comprising the step of: using electrodes for fuel cell obtained with the method described in any one of the above items <13> to <21> as a cathode and/or an anode; and arranging the cathode and/or the anode so as to sandwich an electrolyte therebetween.

<23> In any one of the above items <13> to <22>, the assembly may be a catalyst layer formed on one or both of the electrodes for fuel cell.

[0024]

[Mode for Carrying Out the Invention]

The present invention will be described in detail hereinafter.

An electrode for fuel cell of the present invention is designed in that a proton-conductive polymer is disposed on (for example, covers) a surface (including surfaces of pores) of a porous electron-conductive material carrying a catalyst. The proton-conductive polymer is obtained by polymerizing a proton-conductive monomer or an equivalent thereto in the vicinity of the above-described surface.

[0025]

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The electrode for fuel cell of the present invention can be used as an anode or a cathode with a desired catalyst or the like. Further, the electrode for fuel cell of the present invention can be used in various types of fuel cells, for example, a solid polymer fuel cell, with a desired catalyst or the like. Examples of a fuel for a fuel cell may include, but are not limited to, hydrogen; hydrocarbons such as alcohols represented by methanol, ethers, and ketones; and the like. The electrode for fuel cell of the present invention can be applied to a fuel cell using hydrogen as a fuel, to a direct fuel cell using hydrocarbons as a direct fuel, or to a reforming fuel cell using hydrocarbons after being reformed into hydrogen.

[0026]

The catalyst used in the present invention is not particularly limited as described above, and any catalyst can be used as far as providing desired characteristics. For example, a noble metal catalyst, especially, a catalyst system having a platinum group, and more specifically, Pt, Pt-Ru or the like can be used. Upon using an anode for DMFC, a catalyst is preferably Pt-Ru.

[0027]

The porous electron-conductive material used in the present invention may have an electron conductivity in the range of from 100 to 100,000 S/cm.

The porous electron-conductive material may preferably be a carbon-based porous electron-conductive material. More preferably, examples of the carbon-based porous electron-conductive material may include, but are not limited to, carbon black such as channel black, furnace

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black, acetylene black and Ketjen black (registered trademark), graphite, carbon fiber, carbon nanotube, fullerene, activated carbon, and glass carbon.

[0028]

The porous electron-conductive material may have pores having many three-phase interfaces with a larger surface area. Therefore, the average of pore diameters of the porous electron-conductive material may be, for example, 10  $\mu$ m or less, preferably from 1 nm to 1  $\mu$ m, and more preferably from 1 to 100 nm, but not limited thereto. Furthermore, the average primary pore diameter of carbon black, which is well used as an electrode for fuel cell, is in the range of 10 to 30 nm. Thus, carbon black can be used in the present invention.

[0029]

A proton-conductive polymer provided to the electrode for fuel cell of the present invention is obtained by disposing a proton-conductive monomer in the vicinity of the surface (including surfaces of pores) of the porous electron-conductive material, followed by polymerization. Further, the term "a proton-conductive monomer or an equivalent thereto" may include a monomer and a material which is equivalent thereto in the meaning. The equivalent material means dimer, trimer and the like.

[0030]

Examples of the proton-conductive monomers may include: monomers having a vinyl group, a strong acid group such as a sulfonic or phosphonic group, a weak acid group such as a carboxylic group, or a strong base group such as a primary amine, secondary amine, tertiary amine and



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quarternary amine, or a monomer having a weak base group and a derivative thereof such as an ester in a structure of a molecule such as sodium acrylsulfonate (SAS), sodium methallyl sulfonate (SMS), sodium p styrene sulfonate (SSS), acrylic acid (AA), and others; and allylamine, allylsulfonic acid, allylphosphonic acid, methallylsulfonic acid, methallylphosphonic acid, vinylsulfonic acid, vinylphosphonic acid, styrenesulfonic acid, styrenephosphonic acid, a sulfonic acid or phosphonic acid derivative of acrylamide, ethyleneimine and methacrylic acid. In addition, perfluorosulfonic acid or the like can be used. A monomer matured into a polymer having an ether bond such as polyethylene oxide (for example, ethylene glycol) can be used as well. Furthermore, a salt type such as a sodium salt can also be used as a monomer. In this case, the salts in a polymer matured from a monomer may be preferably transformed into a proton type.

[0031]

In a case where a proton-conductive polymer is formed with the monomers described above, a homopolymer may be formed using only one type of monomer described above, and a copolymer may be formed using two or more types of monomers described above. Further, a copolymer may be formed using monomers other than the above-described ones. In a case where a monomer or monomers other than the monomers described above are used, the monomer or monomers are preferably used to the extent where no proton-conductivity is affected.

[0032]

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The proton-conductive polymer of the present invention is a homopolymer or a copolymer with the monomer described above as a repetition unit. In a case of a copolymer, a monomer or monomers other than the monomers described above can be used.

The proton-conductive polymer of the present invention may be not caused to flow out by a cell power generation operation from the surface of the material, especially from inside pores. For example, the proton-conductive polymer may be not caused to flow out by the action of water from the surface of the material, especially from inside pores. More specifically, one end of the proton-conductive polymer of the present invention may be bound to the surfaces of the pores of the porous electron-conductive material through a chemical bond. Alternatively, the proton-conductive polymer of the present invention may have a hydrophobic site, and the polymer may be adsorbed in a hydrophobic manner to the surfaces of the pores of the porous electron-conductive material via the hydrophobic site. In the latter case, examples of the hydrophobic site may include any of general hydrophobic groups in organic chemistry, but not particularly limited thereto. Furthermore, the term "hydrophobic adsorption" means a tendency in which hydrophobic groups or hydrophobic substances are adsorbed to each other in a surrounding environment constituted of "water" or "hydrophilic material", which is also referred to as "hydrophobic effect", "hydrophobic-medium effect" or "hydrophobic coupling".

[0033]

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The proton-conductive polymer of the present invention may be formed so that one end thereof is bound to the surface (including surfaces of pores) of the material according to the following methods. One of the methods is such that a porous electron-conductive material is excited by, for example, a plasma, ultraviolet, an electron beam or gamma rays so as to generate a reaction start point on the surface (including surfaces of pores) of the material, and bringing the above-described monomer into contact with the reaction start point to thereby obtain a polymer. Another of the methods is such that, after a surface of a porous electron-conductive material is modified, a proton-conductive polymer is coupled to the modified point. Still another of the methods is such that the above-described monomer is disposed on a material surface (including surfaces of pores) and polymerized there to obtain a polymer using a general polymerization method, and thereafter, the obtained polymer is chemically bound to the porous electron-conductive material by using, for example, a coupling agent.

[0034]

Description will be given for an electrode for fuel cell of the present invention with reference to the accompanying drawings.

The electrode for fuel cell of the present invention can be made of primary particles, secondary particles and an assembly thereof, each of which having three-phase interfaces formed on a microscopic scale.

Figures 1(a) to 1(c) are views schematically showing an electrode (100) for fuel cell prepared in a case where carbon black (1) is used as a porous electron-conductive

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material. Figure 1(a) is an enlarged view of a primary particle (6) formed with the carbon black (1) as a center. A Pt catalyst (3) is carried in pores and on a surface of the carbon black (1). A proton-conductive polymer (5) is arranged so as to cover the pores and the surface of the carbon black (1) and the Pt catalyst (3) to thereby form the primary particle (6).

[0035]

Figure 1(b) is a view showing secondary particles (7) formed by clustering the primary particles (6) (in Figure 1(b), encircled with a dotted line) of Figure 1(a). Since each of the primary particles (6) is provided with the proton-conductive polymer, the proton-conductive polymer is also arranged on a surface and inside pores of the secondary particles (7).

[0036]

Figure 1(c) is a view showing an assembly (9) formed by collecting the secondary particles (7) of the carbon black (1) shown in Figure 1(b). Only a part of the secondary particles (7) contained in the assembly (9) is shown in Figure 1(c). The assembly (9) or a form similar thereto is generally used as an electrode for fuel cell. Since three-phase interfaces are formed in the primary particles (on a microscopic scale) as shown in Figure 1(a) and held as they are in the secondary particles (7) and the assembly (9), the obtained electrode for fuel cell may have improved characteristics.

[0037]

The electrode for fuel cell of the present invention may be employed for a fuel cell, for example, a solid

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polymer fuel cell, especially, a methanol fuel cell including a direct methanol solid polymer fuel cell or a reformed methanol solid polymer fuel cell.

[0038]

Brief description will be given for a construction of a fuel cell below.

A fuel cell is, for example, as shown in a conceptual view of a solid polymer fuel cell (20) of Figure 2, constituted of a cathode (21), an anode (23), and an electrolyte (25) sandwiched between the electrodes.

In a case of a methanol fuel cell, a construction may be adopted in which a reformer is placed on the anode electrode side so as to work as a reformed methanol fuel cell.

[0039]

The electrode for fuel cell of the present invention as described above can be produced according to the following process: a) a step of causing a catalyst to be carried on a porous electron-conductive material, b) a step of forming a proton-conductive polymer in the vicinity of a surface, including pores, of the porous electron-conductive material by carrying out polymerization of a proton-conductive monomer, and c) a step of transforming the porous electron-conductive material into an assembly, wherein the steps can be changeable in the order thereof.

[0040]

More specifically, a first process of the method of the present invention may comprise (a  $\rightarrow$  b  $\rightarrow$  c): a) a step of causing a catalyst to be carried on a porous electron-conductive material; thereafter, b) a step of forming a

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proton-conductive polymer in the vicinity of a surface, including pores, of the porous electron-conductive material by carrying out polymerization of a proton-conductive monomer; and then, c) a step of transforming the obtained porous electron-conductive material into an assembly.

[0041]

A second process of the method of the present invention may comprise (a  $\rightarrow$  c  $\rightarrow$  b): a) a step of causing a catalyst to be carried on a porous electron-conductive material; thereafter, c) a step of transforming the obtained porous electron-conductive material into an assembly; and then, b) a step of forming a proton-conductive polymer in the vicinity of a surface, including pores, of the obtained porous electron-conductive material by carrying out polymerization of a proton-conductive monomer.

A third process of the method of the present invention may comprise (b  $\rightarrow$  a  $\rightarrow$  c): b) a step of forming a proton-conductive polymer in the vicinity of a surface, including pores, of a porous electron-conductive material by carrying out polymerization of a proton-conductive monomer; thereafter, a) a step of causing a catalyst to be carried on the obtained porous electron-conductive material; and then, c) a step of transforming the obtained porous electron-conductive material into an assembly.

[0042]

A fourth process of the method of the present invention may comprise (b  $\rightarrow$  c  $\rightarrow$  a): b) a step of forming a proton-conductive polymer in the vicinity of a surface, including pores, of a porous electron-conductive material by carrying out polymerization of a proton-conductive monomer;

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thereafter, c) a step of transforming the obtained porous electron-conductive material into an assembly; and then, a) a step of causing a catalyst to be carried on the obtained porous electron-conductive material.

[0043]

A fifth process of the method of the present invention may comprise (c  $\rightarrow$  a  $\rightarrow$  b): c) a step of transforming a porous electron-conductive material into an assembly; thereafter, a) a step of causing a catalyst to be carried on the porous electron-conductive material, which is a part of the assembly; and then, b) a step of forming a proton-conductive polymer in the vicinity of a surface, including pores, of the porous electron-conductive material by carrying out polymerization of a proton-conductive monomer.

[0044]

A sixth process of the method of the present invention may comprise (c  $\rightarrow$  b  $\rightarrow$  a): c) a step of transforming a porous electron-conductive material into an assembly; thereafter, b) a step of forming a proton-conductive polymer in the vicinity of a surface, including pores, of the porous electron-conductive material, which is a part of the assembly, by carrying out polymerization of a proton-conductive monomer; and then, a) a step of causing a catalyst to be carried on the porous electron-conductive material.

[0045]

Furthermore, the step b) of each of the processes may include a modification step of modifying the surface of the porous electron-conductive material. The modification step

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is preferably inserted before the proton-conductive monomer is disposed in the vicinity of the surface including pores, or after the disposition of the monomer and before the polymer formation. With the modification step adopted, it is possible either to couple a surface of a porous electron-conductive material and a proton-conductive polymer through a chemical bond or to accelerate the coupling. Alternatively, with the modification step adopted, it is possible to accelerate hydrophobic adsorption between a surface of a porous electron-conductive material and a proton-conductive polymer.

[0046]

More specifically, the modification step in a case where the porous electron-conductive material is carbon black, the proton-conductive monomer is acrylamide t-butylsulfonic acid (ATBS,  $\text{CH}_2=\text{CH}-\text{CO}-\text{NH}-\text{C}(\text{CH}_3)-\text{CH}_2-\text{SO}_3\text{H}$ ), and the proton-conductive polymer is polyacrylamide t-butylsulfonic acid (PATBS) can be a step of introducing a methylol group onto the surface of the carbon black.

[0047]

[Examples]

More detailed description will be given for the present invention based on examples, but the present invention is not limited to the examples.

(Example 1)

Carbon black (XC-72, manufactured by Cabot Co.) was used as a porous electron-conductive material. Furthermore, actually used was carbon black carrying 20 wt% Pt (XC-72, manufactured by E-TEK Co.), which was commercially available in a state where Pt was carried on the carbon black.



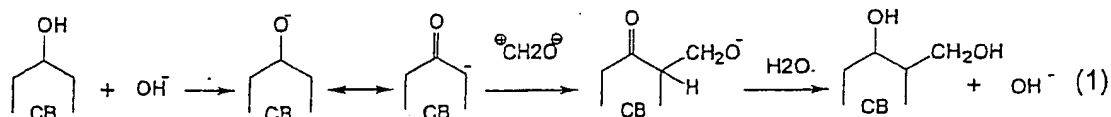
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[0048]

A methylol group was introduced onto the carbon black carrying 20 wt% Pt with the following step (1).

[0049]



[0050]

Specifically, an electrophilic substitution reaction was used based on a method of Fujiki et al., (Kazuhiro FUJIKI et al., Journal of Japan Rubber Society, 64 (6) (1991) 378-385) to introduce a methylol group (-CH<sub>2</sub>-OH) onto surfaces of carbon black. A mixture of carbon black carrying Pt, an aqueous formaldehyde solution and sodium hydroxide was caused to react with each other at 70 °C for 24 hours while being agitated. After the reaction, the resulting substance (carbon black) was filtered out and dried at 100 °C, to obtain a methylol group introduced product A-1.

[0051]

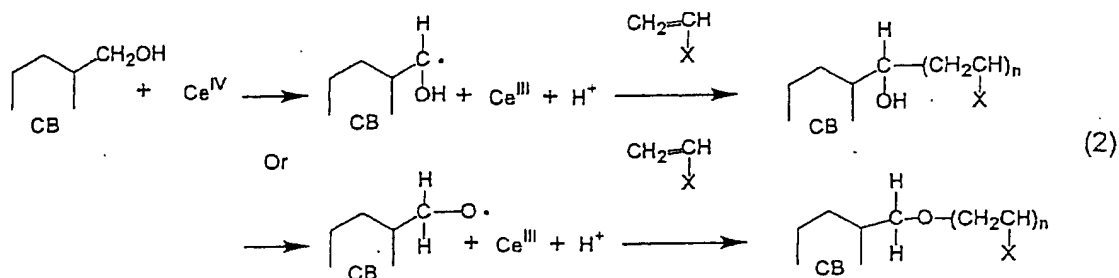
Then, according to the following step (2), a redox polymerization of a proton-conductive polymer was carried out using the methylol groups of the methylol group introduced product A-1 as reaction sites. Used as a proton-conductive monomer was a compound obtained by recrystallizing acrylamide t-butylsulfonic acid (ATBS) in methanol. Furthermore, a proton-conductive polymer PATBS (polyacrylamide t-butylsulfonic acid) having ATBS as a

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repetition unit has higher reactivity and higher sulfonic group content (4.46 mmol/g).

[0052]



[0053]

To be detailed, according to a method of Tsubokawa et al. (N. Tsubokawa et al., J. Macromol. Sci. -Chem. A, 25(9) (1988) 1159-1171), polymer graft polymerization was conducted through redox polymerization in the presence of Ce (IV). Added into a two-necked round-bottomed flask were the methylol group introduced product A-1 and 0.5 mol/L aqueous ATBS monomer solution and further 0.2 mol/L  $\text{Ce}^{4+}$  solution, and the resulting mixture was polymerized at 30 °C with stirring. After the reaction, the polymer was dried in vacuo, to obtain PATBS coupled with carbon black carrying Pt B-1, in which PATBS is coupled with carbon black carrying Pt via methylol groups. Furthermore, the PATBS coupled with carbon black carrying Pt B-1 was subjected to Soxhlet extraction for 24 hours and a non-graft polymer was removed, to isolate the PATBS coupled with carbon black carrying Pt B-1.

It was confirmed from results of an elemental analysis and FT-IR measurement that the PATBS coupled with carbon black carrying Pt B-1 has PATBS polymerized therein. In addition, it was confirmed that Pt activity was retained by cyclic voltammetry measurement.

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[0054]

(Example 2)

Used as a porous electron-conductive material was Ketjen Black carrying 49.1 wt% Pt (Pt, 46.1% on Ketjen Black EC, Lot No. 102-0291, manufactured by Tanaka Noble Metal K.K. and hereinafter referred to as "TEC10E50E"). A methylol group was introduced onto the TEC10E50E in a manner similar to that in Example 1, to obtain methylol-introduced TEC10E50E (A-2).

[0055]

Distilled water was added into the methylol-introduced TEC10E50E (A-2) and the mixture was stirred. A PTFE dispersion (polytetrafluoroethylene 60 wt% dispersion in water, manufactured by Aldrich Co.) was further added therein and stirred, to obtain a paste product D-1. The paste product D-1 was printed on carbon paper (manufactured by TORAY INDUSTRIES, INC.) by means of a screen printing method and the printed carbon paper was dried to obtain an electrode precursor F-1 having a catalyst layer precursor E-1 thereon.

An ATBS monomer solution was introduced onto the catalyst layer precursor E-1 of the electrode precursor F-1 and thereafter, a reaction starting agent solution having cerium (IV) was introduced thereonto to conduct a polymerization reaction in a manner similar to step (2) of Example 1. After the polymerization reaction, the reaction product was subjected to Soxhlet extraction to filter out non-graft polymer having no chemical bond to surfaces of carbon black in the catalyst layer precursor and to thereby obtain a cathode G-1.

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[0056]

An anode H-1 and an electrolyte film I-1 were prepared separately from the cathode G-1. The anode H-1 used was the electrode precursor F-1. The electrolyte film I-1 used was Nafion 112 washed with 1N nitric acid and distilled water.

The electrolyte film I-1 was sandwiched between the cathode G-1 and the anode H-1, and the assembly was hot pressed at 130 °C under 2 MPa for one minute to thereby obtain MEA-1 (MEA: membrane electrode assembly).

[0057]

(Control 1)

MEA-2 of Control 1 was produced so as to have a structure similar to that of MEA-1 of Example 2, except that a cathode was different from that of the MEA-1 of Example 2. That is, the cathode G-2 having electrode precursor F-2 was used, in which the electrode precursor F-2 had a structure similar to the electrode precursor F-1.

[0058]

Data of MEA-1 of Example 2 and MEA-2 of Control 1 are summarized in Table 1.

[0059]

[Table 1]

Table 1: MEA-1 of Example 2 and MEA-2 of Control 1

	Electrolyte film	Anode		Cathode	
		Pt weight (mg/cm <sup>2</sup> )	Graft polymerization	Pt weight (mg/cm <sup>2</sup> )	Graft polymerization
MEA-1	Nafion 112	0.36	None	0.19	Done*
MEA-2	Nafion 112	0.48	None	0.19	None

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\* After a catalyst layer precursor was formed, an ATBS monomer solution was introduced to conduct graft polymerization of poly-ATBS.

[0060]

<Fuel Cell Power Generation Test -Wide Current Density Region->

A fuel cell power generation test (a wide current density region) was conducted using MEA-1 and MEA-2. The test was conducted as follows.

MEA-1 or MEA-2 was set in a PEMFC cell (manufactured by Electro Chem Co.), humidified N<sub>2</sub> gas was flowed through the anode and cathode to thereby humidify both electrodes for 3.5 hours. Thereafter, humidified N<sub>2</sub> gas was changed into H<sub>2</sub> gas at 100 mL/min at the anode and into O<sub>2</sub> gas at 500 mL/min at the cathode, to eventually replace a gas in the cell with a fuel gas. Then, a current at 1000 mA/cm<sup>2</sup> was flowed through the cell. After the system was stabilized, I-V was measured. The I-V measurement was conducted after 3 hours of scanning at a speed of a current density width of 50 mA/cm<sup>2</sup>/30 sec in a region of 0 to 1000 mA/cm<sup>2</sup>. Figure 3 shows results of the test.

[0061]

In Figure 3, the mark ○ indicates MEA-1 and the mark ● indicates MEA-2. MEA-1 (○) exhibits comparatively good power generation performance. Comparison of MEA-1 (○) with MEA-2 (●) shows that Poly-ATBS introduced by graft polymerization plays a role of proton-conduction in a catalytic layer.

[0062]

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(Example 3)

A methylol group introduced TEC10E50E (A-2) was obtained in a manner similar to that in Example 2. After an aqueous ATBS monomer solution was introduced onto the methylol group introduced product (A-2), a starting agent solution was introduced to conduct a polymerization reaction on an oil bath at 35 °C for 48 hours. After the reaction was completed, a reaction product was collected through filtering and dried. In order to further remove a non-graft polymer having no chemical bond to surfaces of carbon black, the dry product was subjected to Soxhlet extraction to obtain a PATBS coupled with carbon black carrying Pt B-2.

[0063]

A catalyst layer E-2 was formed on carbon paper (manufactured by TORAY INDUSTRIES, INC.) as follows.

The PATBS coupled with carbon black carrying Pt B-2 and distilled water were mixed and stirred. Added into the mixture was a Nafion solution (5 wt% solution of Nafion perfluorinated ion-exchange resin containing 15 to 20% water) and the mixture was stirred for about 30 minutes. Further added into the mixture was a PTFE dispersion (60 wt% dispersion in water of Polytetrafluoroethylene, manufactured by Aldrich Co.) and the mixture was stirred, to obtain a catalyst layer paste D-2. The catalyst layer paste D-2 was printed on carbon paper (manufactured by TORAY INDUSTRIES, INC.) by means of a screen printing method and the printed carbon paper was dried, to obtain a cathode G-3.

An electrode and a film having similar structures to those of the anode H-1 and the electrolyte film I-1,

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respectively, were prepared separately from the cathode G-3 to obtain MEA-3 in a manner similar to that in Example 2.

[0064]

(Control 2)

MEA-4 of Control 2 was produced. MEA-4 of Control 2 had a structure similar to that of MEA-2 of Control 1, except that MEA-4 of Control 2 was different in Pt weight from that of MEA-2 of Control 1.

[0065]

Data of MEA-3 of Example 3 and MEA-4 of Control 2 are summarized in Table 2.

[0066]

[Table 2]

Table 2: MEA-3 of Example 3 and MEA-4 of Control 2

	Electrolyte film	Anode		Cathode	
		Pt weight (mg/cm <sup>2</sup> )	Graft polymerization	Pt weight (mg/cm <sup>2</sup> )	Graft polymerization
MEA-3	Nafion 112	0.41	None	0.43	Done*
MEA-4	Nafion 112	0.40	None	0.43	None

\* Before a catalyst layer precursor was formed, an ATBS monomer solution was introduced in a state of carbon black particles to conduct graft polymerization of poly-ATBS.

[0067]

<Fuel Cell Power Generation Test -Low Current Density Region->

A fuel cell power generation test (a low current density region) was conducted using MEA-3 and MEA-4. The test was conducted in the same manner as that in the fuel cell power generation test (wide current density region)

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before the start of I-V measurement and the I-V measurement was conducted in the following way.

The I-V was measured such that a current at 1000 mA/cm<sup>2</sup> was flowed for 10 minutes prior to the I-V measurement conducted after 3 hours of scanning at a speed of a current density width of 10 mA/cm<sup>2</sup>/10 sec in a region of 0 to 100 mA/cm<sup>2</sup>. Results of the test were Tafel plotted (see Figure 4). Furthermore, Tafel equation can be expressed as shown by the following equation (1).

$$\eta = b \log_{10} i_0 - b \log_{10} i \quad \text{..... Equation (1)}$$

In Figure 4, the mark  $\blacklozenge$  indicates MEA-3 and the mark  $\bullet$  indicates MEA-4. Table 3 shows parameters obtained by fitting.

[0068]

[Table 3]

Table 3: Tafel equation parameters of MEA-3 and MEA-4

	$\log_{10} i_0$	$-b$ (V/dec)	$i_0$ (A/cm <sup>2</sup> )
MEA-4	-5.82	0.079	1.5E-06
MEA-3	-5.02	0.092	9.5E-06

[0069]

A "y" intercept of Tafel plotting indicates an exchange current density  $i_0$ . An exchange current density is proportional to an electrode reaction area (three-phase interfaces). Figure 4 and Table 3 show that, when comparing MEA-3 ( $\blacklozenge$ ) with MEA-4 ( $\bullet$ ) with respect to exchange current densities  $i_0$  (y intercept), MEA-3 ( $\blacklozenge$ ) is larger than MEA-4 ( $\bullet$ ). It is suggested that in MEA-3 ( $\blacklozenge$ ), three-phase interfaces increase by graft polymerization, and especially



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a catalyst Pt inside primary pores on carbon black is effectively used. On the other hand, it is suggested that in MEA-4 (●), a catalyst Pt inside primary pores on carbon black is not effectively used.

[0070]

[Effect of the Invention]

According to the present invention, an electrode for fuel cell, for example, an electrode for solid polymer fuel cell, in which three-phase interfaces are efficiently arranged in the electrode and the electrode has improved fuel cell characteristics, can be provided.

Further, according to the present invention, in addition to the above-mentioned effect, a fuel cell having the electrode for fuel cell, for example, a solid polymer fuel cell can be provided.

Furthermore, according to the present invention, in addition to, or other than the above-mentioned effect, a method for producing the electrode for fuel cell and a fuel cell having the electrode therein can be provided.

[Brief Description of Drawing]

[Figure 1] Figures 1(a) to 1(c) are views schematically showing an electrode for fuel cell prepared in a case where carbon black (1) is used as a porous electron-conductive material.

[Figure 2] Figure 2 is a conceptual diagram of a solid polymer fuel cell.

[Figure 3] Figure 3 is a graph showing results of fuel cell tests of MEA-1 of Example 2 and MEA-2 of Control 1.

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[Figure 4] Figure 4 is a graph showing results (Tafel Plotting) of fuel cell tests of MEA-3 of Example 3 and MEA-4 of Control 2.

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[Name of Document] Abstract

[Abstract]

[Object]

To provide an electrode for fuel cell, for example, an electrode for solid polymer fuel cell, in which three-phase interfaces are efficiently arranged in the electrode and the electrode has improved fuel cell characteristics.

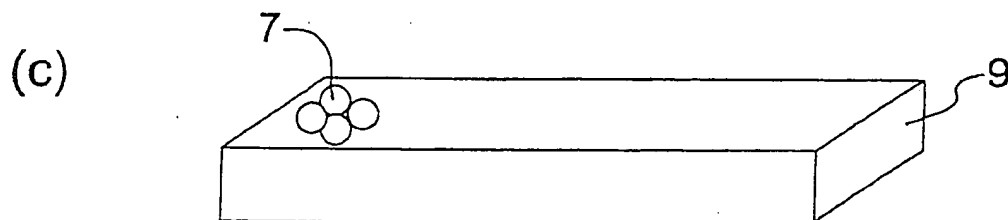
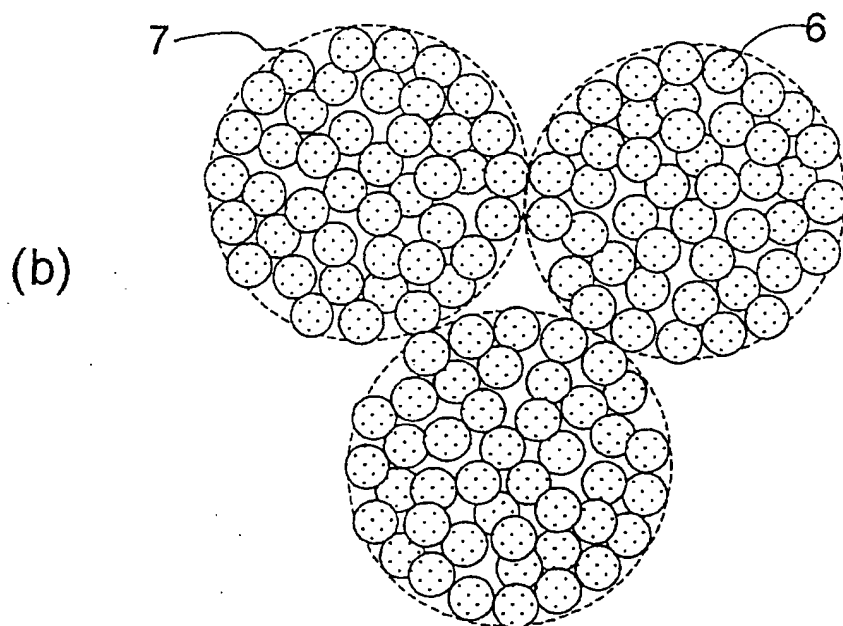
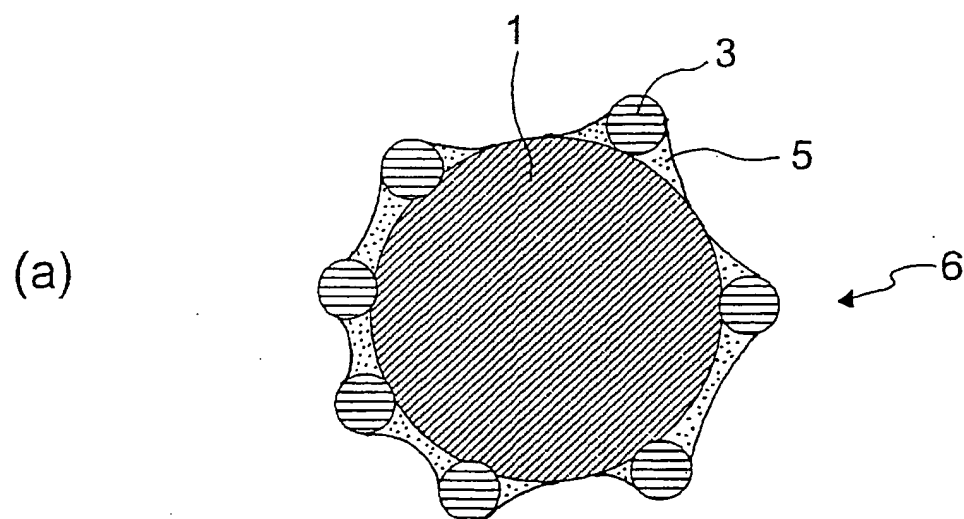
[Means for Solution]

The above-described object is solved by an electrode for fuel cell comprising a porous electron-conductive material carrying a catalyst, wherein a proton-conductive polymer is arranged on a surface, including pores, of the porous electron-conductive material or in the vicinity of the surface, and the proton-conductive polymer is obtained by carrying out polymerization of a proton-conductive monomer or an equivalent thereto on the surface or in the vicinity thereof.

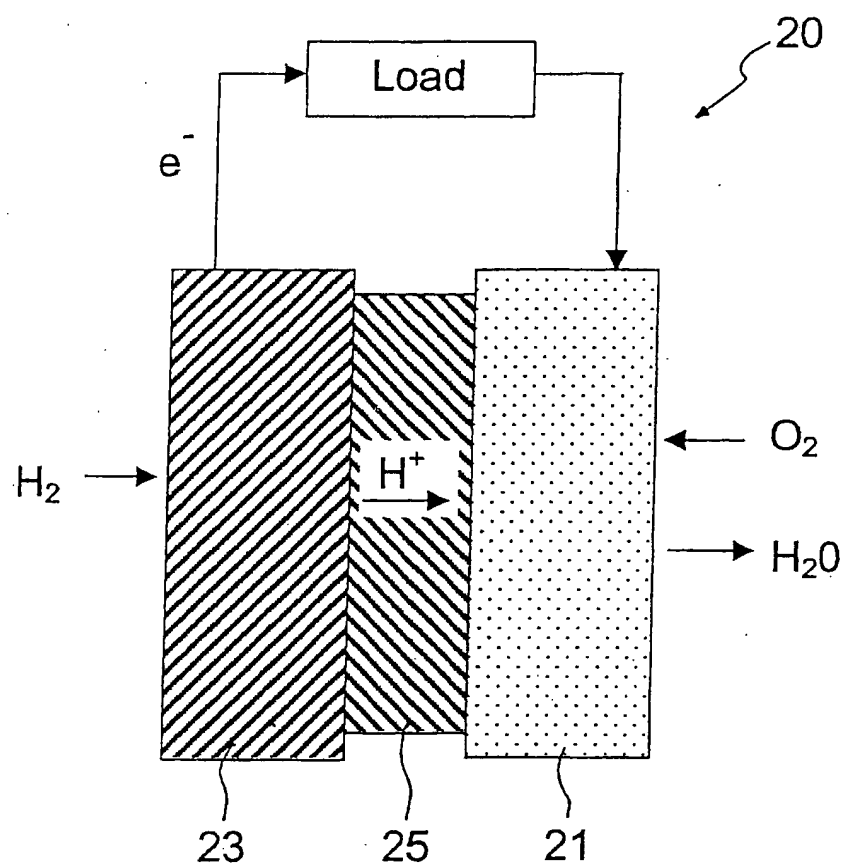
[Selected Drawing] None

【書類名】 図面 Drawings

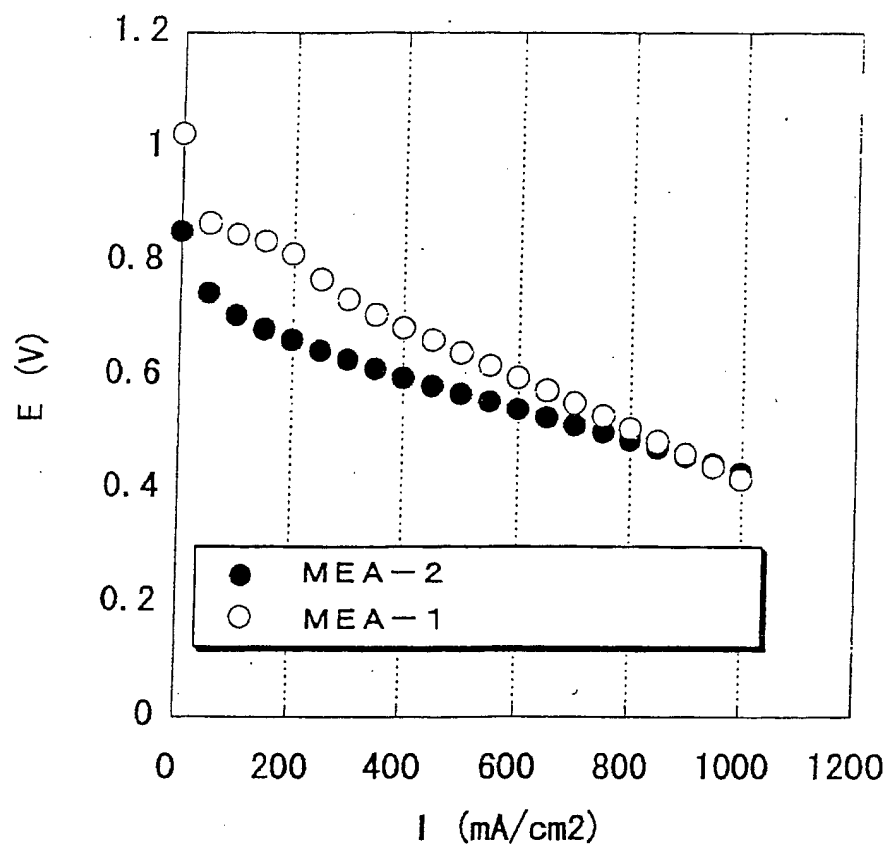
【図1】 Figure 1



【図2】 Figure 2



[図3] Figure 3



【図4】 Figure 4

